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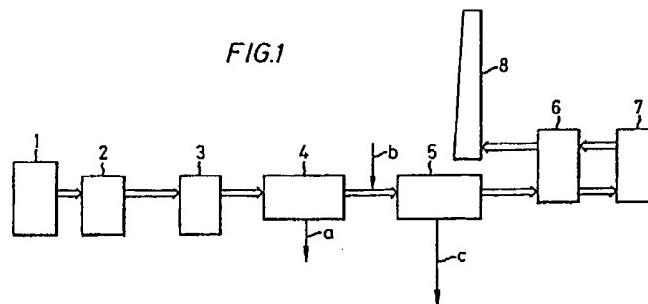
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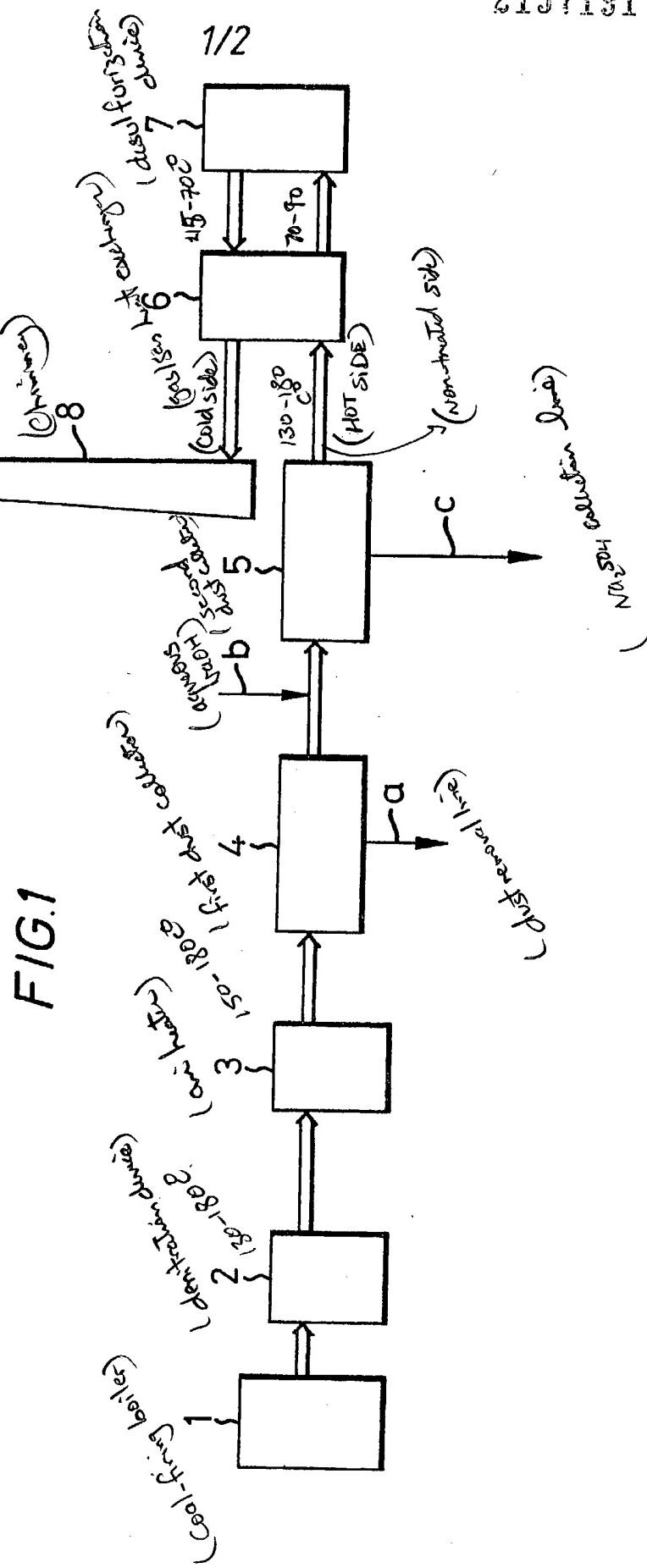
## (54) Removing SO<sub>2</sub> and SO<sub>3</sub> from waste gas

(57) A process for removing dust and sulphur oxides from a combustion waste gas containing them comprises in turn passing the waste gas through a first dust collector (4) to remove dust, spraying into or together with the gas an alkaline suspension and/or aqueous solution (b) to fix SO<sub>3</sub> contained in the waste gas, collecting dry solid from the waste gas by a further dust collector (5) and introducing the waste gas to a wet flue gas desulphurization device (7) to absorb SO<sub>2</sub>. It is convenient to use as the alkaline suspension or aqueous solution waste water from the wet waste flue gas desulphurization device. The waste gas may be that from a boiler (1), may be passed through a denitration device (2), and may be passed through heat exchangers (3), (6) before and after the dust collectors.



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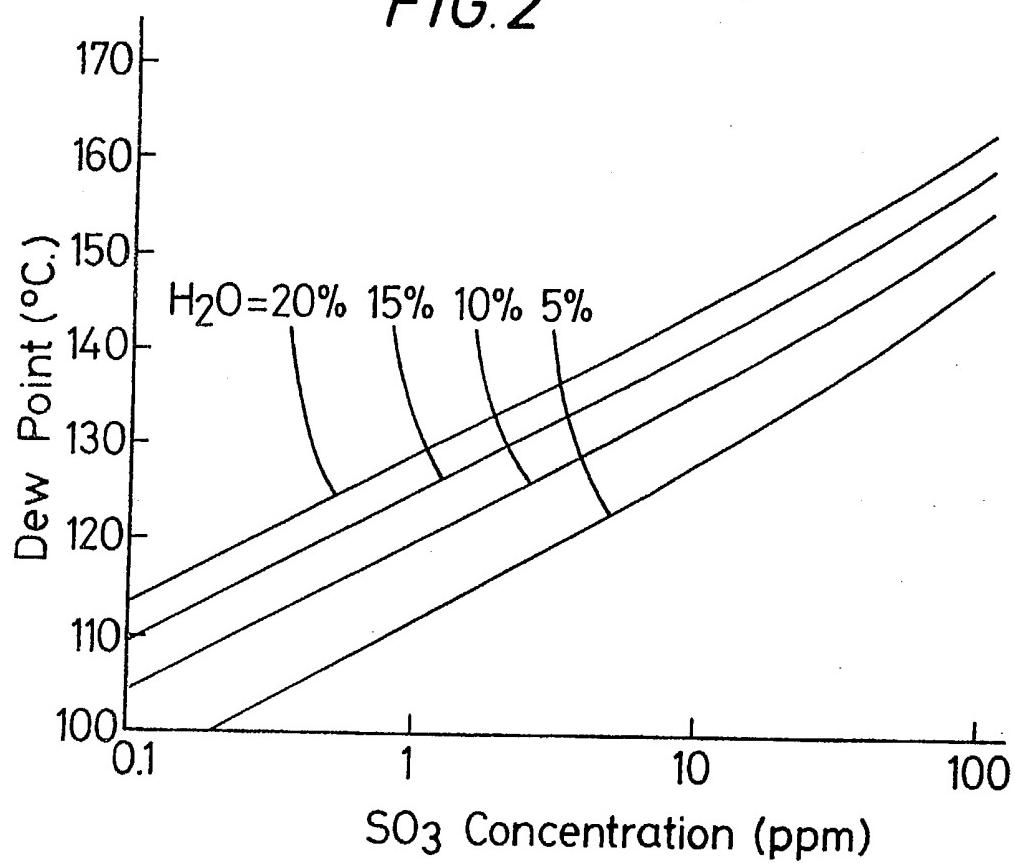
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FIG. 2



## SPECIFICATION

## The removal of dust and sulfuroxide(s) from waste gas

- 5 The present invention is concerned with the removal of dust and sulfuroxide(s) from waste gas and particularly with the treatment of waste gas containing dust and SO<sub>2</sub> and SO<sub>3</sub> (SO<sub>2</sub> and SO<sub>3</sub> are herein generally referred to as SO<sub>x</sub>) such as the waste gas of a coal-fired boiler. 5
- A high-temperature waste gas, for example, a waste gas containing dust and air-polluting substances like nitrogen oxide(s) (NO<sub>x</sub>) and sulfur oxide(s) (SO<sub>x</sub>) such as the waste gas of a coal-fired boiler is generally synthetically treated for disposal by first injecting ammonia (NH<sub>3</sub>) into it then, in a denitration column packed with catalyst, reducing nitrogen oxide in it to water and nitrogen. 10
- Next, using an air heater, heat is recovered from the waste gas to the extent that this is economic, usually reducing the waste gas temperature to 130 - 180°C. The dust is removed by an electrostatic dust collector (precipitator) or cyclone dust collector and thereafter, the waste gas is subjected to a wet desulfurization treatment. 15
- In a typical wet desulfurization process, such as the wet lime gypsum process, the treated gas becomes a gas saturated with moisture at 45 - 70°C. When it is discharged in this form from a chimney there is a problem in that it mixes with the atmosphere, becomes white smoke and is unlikely to diffuse in the atmosphere due to the low temperature. Therefore in practice this low temperature waste gas has been reheated. 20
- Methods of reheating include indirect heating, using a heating medium such as hot water, oil or steam, and direct heating by the use of a heat saver such as a Jungstrom type heat exchanger. However, to save energy the latter has in practice become favoured, in the form of a gas-gas heat exchanger, see Seo et al; "Thermal and Nuclear Power Generation", Vol. 30, No. 2, p.29 - 35 (1979) and "Technological Report" of Mitsubishi Heavy Industries, Ltd. Vol. 17, No. 2, p.217 - 222 (1980). 25
- This gas-gas heat exchange method comprises passing the high temperature (normally 130 - 180°C) influent gas for the wet desulfurization device and the low temperature (normally 45 - 70°C) gas leaving it, to opposite sides of gas-gas exchanger, exchanging heat therebetween. This reduces the temperature of the waste gas immediately before wet desulfurization, so reducing the amount of water needed for humidification and cooling of the gas as a result of the decrease in temperature reduction needed for wet disposal of the waste gas. At the same time, the temperature of the effluent gas from the wet desulfurization device is increased. Therefore this is a so-called energy-saving and natural resources-saving method. 30
- However, because this method depends on a high temperature in the influent gas to the desulfurization device as a heat source, the amount of heat exchanged is dominated by the temperature of the high temperature gas. 35
- When this temperature is rather low, it is incapable of raising sufficiently the temperature of the effluent gas from the wet desulfurization treatment so the discharge from the subsequent chimney still forms smoke. To prevent this the supplementary provision of a steam heater to raise the temperature of the effluent gas after wet desulfurization, as necessary, has been proposed. This, however, is undesirable from the energy-saving point of view. 40
- In addition, elevation of the temperature of the influent gas to the wet desulfurization device, by raising the temperature at the exit of the earlier stage air heater is conceivable. However this causes problems in the following respects.
- In general, a gas discharged from a furnace contains sulfur trioxide (SO<sub>3</sub>) produced by oxidation upon combustion of part of the sulfur content of fuel. Further, as at present, when a denitration device is provided, in the course of the denitration reaction 0.5-4% of any sulfur dioxide (SO<sub>2</sub>) in the gas is oxidized to produce SO<sub>3</sub> in addition to that SO<sub>3</sub> produced in the furnace. Accordingly the amount of SO<sub>3</sub> reaching the entrance of an air heater generally reaches 5-50 ppm as a result of the sulfur content of the fuel. When that SO<sub>3</sub> passes through the air heater, the temperature of the waste gas goes down to below the dew point so that part of the SO<sub>3</sub> gas changes to sulfuric acid mist (H<sub>2</sub>SO<sub>4</sub>) by the following reaction. 45
- SO<sub>3</sub> + H<sub>2</sub>O ⇌ H<sub>2</sub>SO<sub>4</sub>.
- This adheres to accompanying dust and is collected by the later stage collector. However when the temperature at the exit of the air heater is high, due to an equilibrium condition, the condensed amount of H<sub>2</sub>SO<sub>4</sub> due to said reaction is small and the amount of residual SO<sub>3</sub> gas at the exit of the air heater is correspondingly large. Almost all of the SO<sub>3</sub> gas at the exit of the air heater reaches the entrance of the desulfurization device when the temperature of the waste gas is not lowered further. Further, although SO<sub>3</sub> gas becomes H<sub>2</sub>SO<sub>4</sub> mist due to lowering of the temperature when a heat exchanger is used, as described above, the H<sub>2</sub>SO<sub>4</sub> mist produced is very fine and at least some of it may pass through the desulfurization device and be discharged from the chimney, with the fear of causing an acid mat and white smoke. Further there is a high possibility that the materials of construction of the heat exchanger and the desulfurization device will be corroded by H<sub>2</sub>SO<sub>4</sub>. 50
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To prevent such problems, it has been proposed to inject NH<sub>3</sub> to the waste gas at the exit of an oil-burning air heater so as to react it with SO<sub>3</sub> and to form a reaction product of SO<sub>3</sub> and NH<sub>3</sub> (hereinafter referred to as an SO<sub>3</sub>-NH<sub>3</sub> reaction product), such as acidic ammonium sulphate (NH<sub>4</sub>HSO<sub>4</sub>) or ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) which has then been collected by a later-stage collector; "Technological Report of Mitsubishi

5 Heavy Industries, Ltd.," Vol. 10, No. 5, p211-218 (1973).

However, if this method is applied to the removal of SO<sub>3</sub> contained in a waste gas containing a large amount of dust, such as the waste gas from a coal-fired boiler, it is inconvenient because the collection of an NH<sub>3</sub>-SO<sub>3</sub> reaction product and dust leaves the problem of how to dispose of dust mixed with a large amount of the NH<sub>3</sub>-SO<sub>3</sub> reaction product unresolved. Dust from a coal-fired boiler has been effectively utilized as raw material of fly ash cement or it has been dumped, often in land reclamation. In the former case, emission of offensive ammonia odor upon mixing with water and lowering of the cement strength has resulted. In the latter case, emission of offensive ammonia odor and leakage of ammonia to ground water has become a problem. By contrast, in those methods of disposal of waste gases from heavy-oil burning boilers which have been practiced, the amount of dust contained in the waste gas has been extremely small, as compared 10 with that from coal-firing boilers, so the amount of dust mixed with NH<sub>3</sub>-SO<sub>3</sub> reaction product to be disposed has been small enough to present no substantial problem.

15 As a consequence no truly satisfactory process for disposing of a waste gas containing dust and SO<sub>x</sub> has yet been established.

However, we have now found a process for removing, from a waste gas, dust and SO<sub>x</sub> contained therein 20 which comprises passing the waste gas through a first dust collector to remove dust, thereafter spraying into or together with the gas an alkaline suspension or aqueous solution capable of fixing the SO<sub>3</sub> contained in the waste gas, then collecting dry solid from the waste gas by a further dust collector, preferably further heat exchanging the waste gas, and thereafter, introducing the waste gas to a wet flue gas desulfurization device to absorb SO<sub>2</sub> therefrom.

25 By using the process of the present invention, it is possible, even if the temperature of a waste gas at the exit of an air heater is made higher than in the conventional process in an attempt to advance the efficiency of heat exchange at the gas/gas heat exchanger, to avoid the problem of formation of an acid mat and white smoke due to H<sub>2</sub>SO<sub>4</sub> mist and also to avoid corrosion of the materials of the gas/gas heat exchanger and the desulfurization device by H<sub>2</sub>SO<sub>4</sub>. Furthermore the rise in temperature of the waste gas after wet

30 desulfurization disposal can be made sufficient to favour diffusion of waste gas to atmosphere from a chimney.

An important feature of the process of the present invention is the spraying of alkaline suspension or aqueous solution into or with the waste gas after it has passed through a dust collector which has removed dust therefrom. This spraying may be achieved using special spray drying equipment or by means of a spray 35 nozzle inside a duct through which the gas passes.

It is known to desulfurize waste flue gas by a spray drier system: for example Japanese Patent Publication No. 25522/1982 discloses a process for absorbing SO<sub>2</sub> by spray drying an aqueous solution of caustic soda with the hot gas.

We have found that this technique, when applied to the removal of SO<sub>x</sub> by spray drying an aqueous 40 caustic soda solution, when the temperature of a waste gas after spray drying is above 150°C, fixes only SO<sub>3</sub>, while SO<sub>2</sub> is not fixed at all. So, when the waste gas after spray drying is passed through a further dust collector, the solid collected thereby does not contain sulfite which would have become a source of COD. Therefore disposal of this solid can be conveniently achieved.

We have also found that even if the amount of the liquid to be sprayed for removal of SO<sub>3</sub> is small, it is effective to fix SO<sub>3</sub> when the temperature reduction of the gas due to spray drying is not more than 10°C. Advantageously therefore sufficient reheating of the waste gas after wet desulfurization can be achieved by the gas/gas heat exchange method described above.

Application of the process of the present invention to a system for synthetic disposal, rationally combining denitration, dust removing, desulfurization and heat recovery of a waste gas of a coal-fired boiler, makes it 45 possible to raise the temperature of the waste gas at the entrance to the chimney to the necessary temperature in the absence of temperature reduction of the waste gas at the exit of the air heater and without providing further heating, for example by a steam gas heater, at the subsequent gas/gas heat exchange stage. The dust collected by the first dust collector can be reutilized for example in fly ash cement. When the SO<sub>2</sub> is absorbed by a flue gas desulfurization device using the wet lime gypsum method the useful product, 50 gypsum, can be recovered. Furthermore the selective removal of SO<sub>3</sub> by the spray drier method and its subsequent collection by the further dust collector yields a solid which does not contain sulfite to become a source of COD and which is consequently easily disposed of. It is also apparent that troubles at the gas/gas heat exchanger and the desulfurization device due to H<sub>2</sub>SO<sub>4</sub> mist may be avoided.

A preferred embodiment of the invention is described below with reference to the drawings in which Fig. 1 55 is a flow sheet illustrating one method of carrying out the invention and Fig. 2 is an equilibrium diagram of the dew point of H<sub>2</sub>SO<sub>4</sub> and the concentration of SO<sub>3</sub>. This embodiment is described for the purposes of illustration only.

In Fig. 1, a waste gas discharged from a coal-firing boiler 1 is freed from  $\text{NO}_x$  in a denitration device 2, and is therefore fed to an air heater 3. In the denitration device 2, a part of the  $\text{SO}_2$  content of the gas is oxidised to  $\text{SO}_3$  so the amount of  $\text{SO}_3$  at the entrance to the air heater 3 becomes relatively large. For example, for an assumed concentration of  $\text{SO}_2$  of 1000 ppm and assumed oxidation ratios of  $\text{SO}_2$  at the boiler 1 and the 5 denitration device 2 of 1% and 2% respectively, the concentration of  $\text{SO}_3$  at the entrance of the air heater 3 becomes 30 ppm.

The temperature of the waste gas at the exit from the air heater 3 is generally 150 to 180°C. However, as will be apparent from Fig. 2 showing the relationship between the dew point of sulfuric acid and the 10 concentration of  $\text{SO}_3$ , when the temperature of the gas is high, even when the concentration of  $\text{SO}_3$  is large, the temperature of the dew point of sulfuric acid is not reached so that at the exit of the air heater 3, almost all of the  $\text{SO}_3$  remains gaseous.

The waste gas leaving the air heater 3 is next fed to a first dust collector 4, where most of the dust is removed. Ammonia, discharged in a small amount from the denitration device 2, adheres to this dust but since the amount is very small, the dust can be removed from the system through line (a) and effectively

15 utilized for cement or thrown away according to conventional practice. After this dust removal, an aqueous → solution of NaOH is sprayed from a line (b) into the waste gas and  $\text{SO}_3$  in the gas is fixed thereby. Then the waste gas is fed to a further dust collector 5. Normally at least an equimolar amount of NaOH based on  $\text{SO}_3$  is injected and this reacts with  $\text{SO}_3$  to produce  $\text{Na}_2\text{SO}_4$ . The temperature reduction of the waste gas due to this spray drying is at most 10°C.

20 The  $\text{Na}_2\text{SO}_4$  is collected by the second dust collector 5 and is discharged via line (c).

The so treated waste gas is then fed to a gas/gas heat exchanger 6 (on the non-treated side) where its temperature is reduced to 70-90°C. Thereafter, the waste gas is fed to a desulfurization device 7. Since the waste gas fed to the non-treated side of the heat exchanger 6 does not contain  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  mist which would otherwise be produced by temperature reduction of the waste gas inside the heat exchanger 6, is not

25 produced. Accordingly, white smoke is not discharged from chimney 8 and corrosion of the materials of the heat exchanger 6 and the desulfurization device 7 by sulfuric acid can be avoided. The waste gas leaving the desulfurization device 7 is again heated by the heat exchanger 6 (on the treated side) and discharged from chimney 8. In the process of the present invention, the temperature of the waste gas fed to the non-treated

→ side of the heat exchanger 6 may, as mentioned above, be established at maximum 180°C, enabling the 30 temperature of the waste gas treated side of the heat exchanger 6 from the desulfurization device 7 to be raised sufficiently. Accordingly, it is not particularly necessary to provide further heating, for example by a steam gas heater.

As mentioned above, by applying the process of the present invention, it is possible to remove  $\text{SO}_3$  from a waste gas at a relatively high temperature so that the temperature of the waste gas at the entrance to the 35 chimney can be kept high enough while still avoiding corrosion of the materials of the heat exchangers and the desulfurization device by  $\text{H}_2\text{SO}_4$  mist.

A specific embodiment of the process of the present invention will now be described for the purposes of illustration only in the following non-limiting example.

#### 40 Example

To a waste flue gas disposal test apparatus made up according to the flow sheet of Fig. 1, 4000 m<sup>3</sup>/h of waste gas from a coal-fired boiler was supplied. When the conditions of the gas before and after each device of the apparatus were measured, the results as shown in Table 1 were obtained.

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Table 1

Where measurement was done	Measurement items			
	Concentration of dust	Concentration of SO <sub>3</sub> gas	Temperature of the gas	Concentration of SO <sub>2</sub> gas
Entrance to first electric dust collector 4	14100 mg/m <sup>3</sup>	10.2 ppm	175°C	not measured
Exit of the same 4	125 "	9.7 ppm	171°C	1050 ppm
Exit of second electric dust collector 5	30 "	Below 1 ppm	165°C	1050 ppm
Exit of gas gas heater 6 (on the non-treated side)	24 "	Below 1 ppm	86°C	not measured
Exit of desulfurization device 7	15 "	Below 1 ppm	48°C	30 ppm
Entrance to chimney 8	14 "	Below 1 ppm	120°C	not measured

In this example 0.74 mol/l of an aqueous solution of NaOH was injected at a speed of 21 l/h from a spray nozzle to the entrance duct of the second electric dust collector 5. This aqueous solution of NaOH was prepared by dissolving NaOH in the waste water from the waste flue gas desulfurization device 7 using the wet lime gypsum method. This meant that waste water disposal became unnecessary. The amount of corrosion inferred from the weight loss of a SS-41 test piece set up in the flue at the exist of the gas gas heater 6 (on the non-treated side) was less than 0.01 mm/yr and from visual observation also, an inclination to corrode was hardly detected.

*Comparative Test*

The example was repeated except that the injection of aqueous NaOH solution to the entrance of the second dust collector was discontinued. The conditions of the waste gas before and after the respective devices were measured to obtain the results shown in Table 2.

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Table 2

Where measurement was done	Measurement items		
	Concentration of dust	Concentration of SO <sub>3</sub> gas	Temperature of the gas
Entrance to first electric dust collector 4	14500 mg/m <sup>3</sup> N	10.1 ppm	175°C
Exit of the same 4	130 "	9.8 ppm	171°C
Exit of second electric dust collector 5	35 "	9.5 ppm	170°C
Exit of gas/gas heater 6 (on the non-treated side)	22 "	Below 1 ppm	90°C
Exit of desulfurization device 7	20 "	Below 1 ppm	48°C
Entrance to chimney 8	16 "	Below 1 ppm	123°C

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The amount of corrosion calculated from the weight loss of an SS-41 test piece set up in the flue at the exit of the gas/gas heat exchanger 6 (on the non-treated side) was 1.6 mm/yr and visual observation also indicated recognisable corrosion.

60 The Example and Comparative Test demonstrate the unexpected effect of injection of the aqueous NaOH solution to the entrance to the second dust collector 5. 60

## CLAIMS

1. A process for removing dust and sulfur oxide(s) from a combustion waste gas containing them which comprises passing said waste gas through a first dust collector (4) to remove dust, subsequently spraying 5 into or together with the gas an alkaline suspension and/or aqueous solution capable of fixing the SO<sub>3</sub> contained in the waste gas, subsequently collecting dry solid from the waste gas by a further dust collector (5) and subsequently introducing said waste gas to a wet flue gas desulfurization device (7) to absorb SO<sub>2</sub>. 5
2. A process as claimed in claim 1, wherein waste water coming from said wet waste flue gas 10 desulfurization device is utilized as the alternative suspension or aqueous solution. 10
3. A process as claimed in Claim 1 or 2, wherein the spraying step comprises spray drying the waste gas with the alkaline suspension and/or aqueous solution. 10
4. A process as claimed in Claim 3 wherein the temperature reduction of the gas, as a result of the spray drying alkaline suspension or aqueous solution, is not more than 10°C.
- 15 5. A process as claimed in Claim 3 or 4, wherein the temperature of the waste gas, after spray drying, is above 150°C. 15
6. A process for removing dust and sulfur oxide(s) from combustion waste gas, substantially as hereinbefore described with reference to the accompanying drawings.

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